

Scattering intensity limit value at very small angles

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Abstract

The existence of the limit of a sample scattering intensity, as the scattering vector approaches zero, requires and is ensured by the property that the mean value of the scattering density fluctuation over volume V asymptotically behaves, at large V s, as $\nu V^{-1/2}$, ν being an appropriate constant. Then, the limit of the normalized scattering intensity is equal to ν^2 . The implications of this result are also analyzed in the case of samples made up of two homogeneous phases.

Synopsis: The mean value of the scattering density fluctuation must asymptotically behave as $V^{-1/2}$ for the scattering intensity limit at reciprocal space origin to exist.

Keywords: small angle scattering intensity, very small angle limit, scattering density fluctuation, large volume behavior of the fluctuation mean

Introduction

The aim of this note is to discuss the existence as well as the meaning of $I(0^+)$, *i.e.* the limit of $I(\mathbf{q})$, the elastic scattering intensity of X-rays or neutrons, as the modulus (q) of the scattering vector (\mathbf{q}) approaches zero. It is well known that $I(0^+)$ is linearly related to the isothermal compressibility of the sample if this is a fluid made up of identical particles [Guinier & Fournet (1955), Hansen & MacDonald (1976)]. Oppositely, to the author knowledge, no general expression was known in the case of sample made up of two homogeneous phases (as it is commonly assumed in the small-angle scattering realm) till a recent paper by Gommès (2006) who showed that $I(0^+)$ is equal to the variance of the scattering density fluctuation under the assumption that this consists of a collection of independent and equally distributed random variables (Rosenthal, 2000).

Aim of this note is to point out a different interpretation of $I(0^+)$, namely: the integral of a physical scattering density fluctuation over a volume V , at large V s, asymptotically behaves as $\nu V^{1/2}$ where the numerical coefficient ν is related to the $I(0^+)$ value by the simple relation $I(0^+) = \nu^2$.

To begin with, it is convenient first to recall a basic assumption usually understood in dealing with the scattering experiment results from a matter sample: no change is experimentally observable if one varies the volume V as well as the center of gravity position O of the sample's illuminated portion V_O with respect to the ingoing beam and/or if one cuts another sample from a given material specimen. [For a discussion of these aspects in the case of stereological analysis one should refer to a report by Lantuejoul (1990).] The expression of the scattering intensity $\mathcal{I}_{V_O}(\mathbf{q})$, relevant to a sample illuminated volume V_O , is simply given by [Guinier & Fournet (1955), Kostorz (1979), Feigin & Svergun (1987)]

$$\mathcal{I}_{V_O}(\mathbf{q}) = |\tilde{n}_{V_O}(\mathbf{q})|^2, \quad (1)$$

where $\tilde{n}_{V_O}(\mathbf{q})$ denotes the Fourier transform (FT) of $n_{V_O}(\mathbf{r})$, the scattering density of the illuminated portion of the sample. This function is defined as being equal to $n(\mathbf{r})$ (the scattering density of the infinitely large sample) if the tip of \mathbf{r} falls inside V_O , the sample illuminated part having its gravity center set at point O , and to zero elsewhere. It is also recalled that the $n(\mathbf{r})$ determination requires a statistical mechanical average or the use of the functional density theory since the only small angle scattering intensity is not sufficient for its determination. Even though a Dirac $\delta(\cdot)$ -like approximation of $n(\mathbf{r})$ is sometimes adopted in the case of perfect crystals, it will be assumed, in the first part of this note, that $|n(\mathbf{r})|$ is a continuous bounded function and, in the second, that it is a discrete valued function. The $n(\mathbf{r})$ and $n_V(\mathbf{r})$ units

are L^{-3} and L^{-2} in the case of X-ray and neutron scattering, respectively. Moreover, the $\mathcal{I}_{V_O}(\mathbf{q})$ definition refers to an ingoing beam of unit intensity and it also understands that the electron Thomson factor, present in the only case of X-ray scattering, be factorized out. We explicitly restate now the two assumptions on which the following analysis rests:

- A) the scattering density is either a continuous or a discrete valued function, in both cases with lower and upper finite bounds. This assumption clearly confines the scattering vector to the small-angle domain and excludes fractal systems from our analysis;
- B) once V is larger or of the size considered in scattering experiments, the *observed* scattering intensity per unit volume $I_{V_O}(\mathbf{q}) = \mathcal{I}_{V_O}(\mathbf{q})/V$ is independent on V and on O , which justifies the standard notations $I(\mathbf{q})$ and $\mathcal{I}(\mathbf{q})$.

The continuous scattering density case

Equation (1) implies that

$$\mathcal{I}_{V_O}(0) = \bar{n}_{V_O}^2 V^2, \quad (2)$$

where \bar{n}_{V_O} denotes the mean value of $n(\mathbf{r})$ over V_O . Guinier & Fournet(1955) (hereafter referred to as I) already stressed that this mean value differs from $\bar{n}[\equiv \lim_{V \rightarrow \infty} (\int_V n(\mathbf{r}) d\mathbf{v}/V)]$, the mean scattering density value of the infinitely large sample. Similarly to what reported in section 2 of Landau & Lifshitz (1967a), let us assume now that, as V_O gets larger and larger, \bar{n}_{V_O} asymptotically behaves as

$$\bar{n}_{V_O} \approx \bar{n} + \nu_o/V^{1/2} + \nu_o'/V^\epsilon \quad (3)$$

with $\epsilon_o > 1$ and ν_o and ν_o' suitable constants, eventually depending on the position O . In this way, by (2), one would find that

$$\mathcal{I}_{V_O}(0) \approx \bar{n}^2 V^2 + 2\bar{n} \nu_o V^{3/2} + \nu_o^2 V + \dots \quad (4)$$

This relation shows that $\mathcal{I}_V(0)$, similarly to the intensity values observed at the Laue spots in the case of crystalline samples (Landau & Lifshitz, 1967b), scales as V^2 provided V is sufficiently large. But, in contrast with the intensity values at the Laue spots [different from $(0, 0, 0)$], the $\mathcal{I}_V(0)$ value is experimentally not observable due to the beam stop presence. Hence, the value of the scattering intensity at the origin of reciprocal space can only be obtained extrapolating the collected $\mathcal{I}_{V_O}(\mathbf{q})$ values towards the origin.

However, according to B), for the \mathbf{q} s lying outside the beam stop $I_{V_O}(\mathbf{q})$ behaves as an intensive quantity, also independent on O , once V is not smaller than the size usually employed in experiments. Therefore, assuming that the aforesaid extrapolation procedure be unambiguous and denoting the resulting value by $\mathcal{I}_{V_O}(0^+)$, the requirement that the $O(V)$ contribution present (4) continuously matches the extrapolated one yields

$$I_{V_O}(0^+) = \mathcal{I}_{V_O}(0^+)/V \approx \nu^2, \quad (5)$$

i.e. the $q \rightarrow 0$ limit value of the scattering intensity per unit volume of the illuminated sample is determined by the coefficient of the $O(V^{-1/2})$ term present in the \bar{n}_V asymptotic expansion. This, moreover, must have the form reported in (4) with ν independent on O , as we already wrote in (5). To make the above argument rigorous one needs to show that $\mathcal{I}_V(q)$ shows up a peak that fully lies behind the beam stop and that the peak value, as V increases, behaves according to (4). This point is thoroughly explained in I, and we simply mention the main steps. In order to separate the peak contribution, one introduces the so-called scattering density fluctuations $\eta(\mathbf{r})$ of the infinitely large sample according to the definition

$$\eta(\mathbf{r}) \equiv n(\mathbf{r}) - \bar{n}. \quad (6)$$

The scattering density fluctuation of the illuminated part of the sample will be denoted by $\eta_{V_O}(\mathbf{r})$ and, similarly to $n_{V_O}(\mathbf{r})$, it coincides with $\eta(\mathbf{r})$ inside the illuminated portion of the sample and is equal to zero elsewhere so as to write

$$n_{V_O}(\mathbf{r}) = \eta_{V_O}(\mathbf{r}) + \bar{n} \Theta_{V_O}(\mathbf{r}), \quad (7)$$

where $\Theta_{V_O}(\mathbf{r})$ is defined as being equal to 1 if the tip \mathbf{r} falls inside the illuminated part V_O of the sample and to zero elsewhere. By Fourier transforming (7), substituting the result in (1) and recalling that $\mathcal{I}_{V_O}(\mathbf{q}) = V I_{V_O}(\mathbf{q})$ one gets

$$I_{V_O}(\mathbf{q}) = \left[\bar{n}^2 |\tilde{\Theta}_{V_O}(\mathbf{q})|^2 + 2\text{Re}(\tilde{\Theta}_{V_O}(\mathbf{q}) \overline{\tilde{\eta}_{V_O}(\mathbf{q})}) \right] / V + |\tilde{\eta}_{V_O}(\mathbf{q})|^2 / V. \quad (8)$$

[Here the large overbar denotes the complex conjugate and the tilde the FT.] As explained in I, the contribution inside the square brackets is restricted to an angular range fully hidden by the beam-stop once V has approached a size two-three order of magnitudes smaller than that employed in typical experiments. Besides, it approaches to a Dirac δ function as $V \rightarrow \infty$. Hence, it does not contribute to the limit of the observed $I_{V_O}(\mathbf{q})$ as $q \rightarrow 0$ and

$I_{V_O}(0^+)$ is fully determined by the limit of the second term on the rhs of (8). In conclusion, the large value of V makes it accurate to write, for $q > 0$,

$$I_{V_O}(\mathbf{q}) = |\tilde{\eta}_{V_O}(\mathbf{q})|^2/V = \int_{R^3} e^{i\mathbf{q}\cdot\mathbf{r}} \gamma_{V_O}(\mathbf{r}) d\mathbf{v}, \quad (9)$$

where $\gamma_{V_O}(\mathbf{r})$, the non-normalized correlation function of the sample, is defined as

$$\gamma_{V_O}(\mathbf{r}) \equiv \frac{1}{V} \int \eta_{V_O}(\mathbf{r}_1) \eta_{V_O}(\mathbf{r}_1 + \mathbf{r}) d\mathbf{v}_1. \quad (10)$$

The $\mathbf{q} \rightarrow 0$ limit of (9) yields

$$\begin{aligned} I_{V_O}(0^+) \approx I(0^+) &= \lim_{V \rightarrow \infty} |\tilde{\eta}_{V_O}(0)|^2/V = \lim_{V \rightarrow \infty} \left[\int_{R^3} \gamma_{V_O}(\mathbf{r}) d\mathbf{v} \right] = \\ &= \lim_{V \rightarrow \infty} \left[\int \eta_{V_O}(\mathbf{r}) d\mathbf{v} / V^{1/2} \right]^2. \end{aligned} \quad (11)$$

By construction, the scattering density fluctuation definition (6) implies that its mean value $\bar{\eta}$ is equal to zero, *i.e.* $\bar{\eta} \equiv \lim_{V \rightarrow \infty} (\int \eta_{V_O}(\mathbf{r}) d\mathbf{v} / V) = 0$. It is noted that this limit value does not imply that $\lim_{V \rightarrow \infty} \int \eta_{V_O}(\mathbf{r}) d\mathbf{v} = 0$. In fact, for the first limit to be valid, it is necessary and sufficient that, at large V s, one asymptotically finds

$$\left| \int \eta_{V_O}(\mathbf{r}) d\mathbf{v} \right| \approx |\nu_o| V^\alpha \quad \text{with} \quad \alpha < 1, \quad (12)$$

and ν_o constant. Substituting this behavior into the rightmost member of (11) one finds that the quantity inside the square brackets behaves as $\nu_o^2 V^{2\alpha-1}$. Since we are in a V range where assumption B) applies, $I_V(0^+)$ is intensive with respect to V and, for this to happen, it must result $2\alpha - 1 = 0$, *i.e.* $\alpha = 1/2$. Then, equation (12) becomes

$$\left| \int \eta_{V_O}(\mathbf{r}) d\mathbf{v} \right| \approx |\nu| V^{1/2}, \quad (13)$$

where assumption B) again requires that $|\nu|$ does not depend on O that was therefore omitted as suffix. In appendix A we show that the above equation coincides with

$$\int \eta_{V_O}(\mathbf{r}) d\mathbf{v} \approx \nu V^{1/2}, \quad (14)$$

if one assumes that $\nu \neq 0$ and we also report an example of function obeying condition (14). Using definition (6), one immediately realizes that condition (14) coincides with a weakened form of (3) in so far the condition $\epsilon > 1$ is now

substituted by $\epsilon > 1/2$ because $\bar{\eta} = 0$. Besides, it is not necessary to assume the validity of the weakened (3) because this condition is a consequence of the intensive nature of $I_{Vo}(0^+)$ with respect to V . The basic conclusion of this analysis follows from equations (14) and (11). It states that: the $\mathbf{q} \rightarrow 0$ limit of the scattering intensity is equal to the squared coefficient in front of the leading $O(V^{-1/2})$ term of the asymptotic expansion of the mean value of the scattering density fluctuation as $V \rightarrow \infty$, *i.e.*

$$I_V(0^+) \approx I(0^+) = \nu^2. \quad (15)$$

This quantity is certainly positive and varies within the range $[0, \infty)$, the outermost values being clearly assumed in the proximity of possible critical points. It is also noted that the ν^2 units are $[L^{-3}]$ for X-ray scattering and $[L^{-1}]$ for neutron one.

From equation (14) it is possible to derive a further consequence of some interest, namely: the angular average of the scattering density fluctuation, at fixed distance r from a point O , decreases as $r^{-3/2}$, whatever O , at very large rs . More precisely, one has

$$\frac{1}{4\pi} \int \eta(r\hat{\omega}) d\hat{\omega} \approx \frac{\nu}{2\sqrt{3}(4\pi r)^{3/2}}. \quad (16)$$

[Here $\hat{\omega}$ denotes a unit vector that spans all possible directions.] To prove this relation, consider a spherical shell \mathcal{S} of center O , thickness δ and inner radius r . Denote by V_1 and V_2 the spheres centered at O and having radii equal to r and $r + \delta$ and assume that the spheres are sufficiently large to make (14) valid. It results that

$$\int_{\mathcal{S}} \eta(\mathbf{r}) d\mathbf{v} = \int \eta_{V_2} d\mathbf{v} - \int \eta_{V_1} d\mathbf{v} \approx \nu(V_2^{1/2} - V_1^{1/2})$$

The difference of the two integrals, evaluated up to terms $O(\delta)$, is equal to $4\pi r^2 \delta \int \eta(r\hat{\omega}) d\hat{\omega}$, while $V_2^{1/2} - V_1^{1/2} \approx (4\pi r^3/3)^{1/2} \delta/2r$. By these two expressions one immediately recovers result (16).

Relation (14) is fully general and represents the basic result of this note.

The discrete valued scattering density case

We analyze now the implications of (14) when one assumes that the scattering density fluctuation has the form pertinent to a two homogeneous phase sample [Debye *et al.* (1957), Ciccariello(2002)], the case most typically considered in the small-angle scattering realm. As customary, we denote by $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ the characteristic functions of phases 1 and 2 that respectively have

scattering density values equal to n_1 and n_2 . [We also recall that $\rho_1(\mathbf{r})$ is, by definition, equal to 1 if the tip of r falls inside phase 1 and to 0 elsewhere. The definition of $\rho_2(\mathbf{r})$ is perfectly similar.] The scattering density of the infinitely large sample takes now the form: $n(\mathbf{r}) = n_1\rho_1(\mathbf{r}) + n_2\rho_2(\mathbf{r})$. The volume fraction φ_1 of phase 1 is given by the relation $\varphi_1 = \lim_{V \rightarrow \infty} (\int_V \rho_1(\mathbf{r}) dv / V)$ and is, therefore, equal to the mean value of $\rho_1(\mathbf{r})$. The volume fraction φ_2 of phase 2 is similarly defined. Since $\rho_1(\mathbf{r}) + \rho_2(\mathbf{r}) \equiv 1$, one has $\varphi_1 + \varphi_2 = 1$. By the above relations one immediately finds that the mean scattering density value, relevant to the infinitely large sample, is $\bar{n} = n_1\varphi_1 + n_2\varphi_2$. The scattering density fluctuation takes the form

$$\begin{aligned} \eta(\mathbf{r}) &= (n_1 - \bar{n})\rho_1(\mathbf{r}) + (n_2 - \bar{n})\rho_2(\mathbf{r}) = \\ &= (n_1 - n_2)\varphi_2\rho_1(\mathbf{r}) - (n_1 - n_2)\varphi_1\rho_2(\mathbf{r}). \end{aligned} \quad (17)$$

The existence of $I_V(0^+)$, by the same considerations reported above equation (15) and the observation that the integral of $\eta(\mathbf{r})$ over V_O continuously depends on V and O , requires and is ensured by the following asymptotic behavior

$$\left| \int_{V_O} \eta(\mathbf{r}) dv \right| \approx |(n_1 - n_2) \rho| V^{1/2}, \quad (18)$$

where ρ is a constant with dimensions $[L^{3/2}]$. Using (17) and the properties $\rho_2(\mathbf{r}) = 1 - \rho_1(\mathbf{r})$ and $\varphi_1 + \varphi_2 = 1$, the above integral converts into

$$\begin{aligned} \left| \int_{V_O} \eta(\mathbf{r}) dv \right| &= |n_1 - n_2| \left| \left[(\varphi_1 + \varphi_2) \int_{V_O} \rho_1(\mathbf{r}) dv - \varphi_1 V \right] \right| = \\ &= |n_1 - n_2| \left| \int_{V_O} (\rho_1(\mathbf{r}) - \varphi_1) dv \right|. \end{aligned} \quad (19)$$

The comparison of (19) to (18) yields

$$\int_{V_O} \rho_1(\mathbf{r}) dv \approx \varphi_1 V + \rho V^{1/2}, \quad (20)$$

because the absolute value can be omitted proceeding as in appendix A. Then, equation (18) can be recast in the form

$$\int_V \eta(\mathbf{r}) dv \approx (n_1 - n_2) \rho V^{1/2}. \quad (21)$$

If condition (21) is obeyed, one finds that

$$I_V(0^+) = \nu^2 = (n_1 - n_2)^2 v_0 \quad \text{with} \quad v_0 \equiv \rho^2. \quad (22)$$

Since v_0 has the dimension of a volume, the above relation shows that the $\mathbf{q} \rightarrow 0$ limit of the observed scattering intensity is equal to the phase contrast times a typical volume that, in turns, is the square value of the coefficient of the $O(V^{1/2})$ term in the asymptotic expansion of the integral of the characteristic function of one of the sample phases.

We have already emphasized that the existence of $I_V(0^+)$ constraints $\eta(\mathbf{r})$ to be such that its integral over V asymptotically behaves as reported in equation (14) or as in equation (21) in the case of two homogenous phase samples. In the last case, the constraint can further more be elaborated. To this aim, generalizing the approach of Méring and Tchoubar (1968), we partition the infinitely large sample into a sequence of nested hollow spheres \mathcal{S}_i (with $i = 1, 2, \dots$) of equal volume V_0 . We denote by R_i the inner radius of \mathcal{S}_i and, of course, we set $R_1 = 0$ because \mathcal{S}_1 is a sphere. The thickness δ_i of \mathcal{S}_i is given by $\delta_i = (3V_0/4\pi + R_i^3)^{1/3} - R_i$ that, for $i = 1$, yields $\delta_1 = (3V_0/4\pi)^{1/3}$. Since $R_2 = \delta_1$ and $R_i = R_{i-1} + \delta_i$ if $i \geq 2$, one can recursively determine all the R_i s and δ_i s. We denote now by v_i the volume of the portion of \mathcal{S}_i that is occupied by phase 1. Then, if V is taken equal to the set occupied by the first N hollow spheres, one finds that

$$\int_V \rho_1(\mathbf{r}) dv = N \left(\frac{1}{N} \sum_{i=1}^N v_i \right) \quad (23)$$

We denote by \bar{v} the limit of the arithmetic mean present within the brackets on the rhs of (23) as $N \rightarrow \infty$. Recalling (20), it clearly results that $\bar{v} = \varphi_1 V_0$. Then, adding and subtracting \bar{v} to each v_i on the rhs of (23) and setting $\xi_i \equiv (v_i - \bar{v})$, the equation converts into

$$\int_V \rho_1(\mathbf{r}) dv = \varphi_1 V + \sum_{i=1}^N \xi_i. \quad (24)$$

The comparison of this relation to (20) shows that the sum on the rhs must behave as $\rho V^{1/2} = \rho(NV_0)^{1/2}$, *i.e.*

$$\sum_{i=1}^N \xi_i \approx \rho V_0^{1/2} N^{1/2}. \quad (25)$$

Squaring one finds

$$\left[\sum_{i=1}^N \xi_i \right]^2 = \sum_{i=1}^N \xi_i^2 + 2 \sum_{1 \leq i < j \leq N} \xi_i \xi_j \approx \rho^2 V_0 N. \quad (26)$$

The ξ_i s can be looked at as a sequence of random numbers with arithmetic mean value equal to zero. Consequently, the sum involving the ξ_i^2 s in the middle of (26), once it is divided by N , yields the variance of the random sequence in the limit $N \rightarrow \infty$. We assume that this variance is finite and we denote its value by $\mu^2 V_0$. This assumption amounts to asymptotically write

$$\sum_{i=1}^N \xi_i^2 \approx \mu^2 V_0 N. \quad (27)$$

Then, the validity of (26) requires that

$$\sum_{1 \leq i < j \leq N} \xi_i \xi_j \approx \mu' V_0 N \quad \text{with} \quad \mu' \equiv \rho^2 - \mu^2. \quad (28)$$

The sum present in (28) involves $N(N-1)/2$ addends. Thus, while in the case of (27) it is sufficient to assume that the ξ_i^2 s have a finite upper bound for the equation to be true, to work out the constraints that make equation (28) valid is not simple. In appendix B we report some examples of random sequences that respectively obey none of (27) and (28) or one of these or both. This result further confirms the conclusion that: a sequence of v_i s is physically realizable [*i.e.* the v_i s form the volume sequence of one of the two homogeneous phases of a real sample] if the associated ξ_i s obey both (27) and (28) because only in this case the $I_V(0^+)$ exists and is intensive with respect to V . In conclusion, we can state: (C) *the sum $\sum_{i=1}^N \xi_i$ asymptotically behaves as $N^{1/2}$, times a constant of dimensions $[L^{3/2}]$, if the random sequence of the ξ_i s has mean value equal to zero, finite variance and obeys (28). The intensity limit value, in terms of the last quantities, reads*

$$I_V(0^+) \approx I(0^+) = (n_1 - n_2)^2 (\mu^2 + \mu') = (n_1 - n_2)^2 \rho^2. \quad (29)$$

We also add the following remarks:

- i) statement C) is similar to the central limit theorem (Rosenthal, 2000). This theorem states that the sum of N independent and identically distributed random variables asymptotically behaves, in distribution, as $N^{1/2}$ times the normal distribution. Hence, in comparison to the central limit theorem, statement C) substitutes the convergence in distribution with the asymptotic convergence and the assumption of independent and identically distributed random variables with conditions (27) and (28);
- ii) in deriving (29) no bounds on the particle size, shape and polydispersity were required. Assuming the sample made up of a single kind of particles, it is possible to relate the $I_V(0^+)$ value [Guinier & Fournet (1955), Hansen & McDonald (1976), Luzzati (1995)] to the isothermal compressibility of the

sample. The last quantity is related to the mean square fluctuation of the particle number (Landau & Lifshitz, 1967, Sect. 114). Interestingly this result can simply be obtained by slightly changing the procedure expounded above equation (23) to account for the hypothesis that each particle is rigid and has volume v_p . To this aim, it is first observed that each particle has its gravity center inside one and only one of the \mathcal{S}_i s. Then the (outer) border of \mathcal{S}_1 is as slightly as possible modified so as the new \mathcal{S}_1' has still volume V_0 , fully contains all the particles having their gravity centers lying within \mathcal{S}_1 and fully excludes those with their centers lying outside \mathcal{S}_1 . We denote by N_1' the number of particles present in \mathcal{S}_1' . The substitution of \mathcal{S}_1 with \mathcal{S}_1' will clearly require the change of \mathcal{S}_2 into \mathcal{S}_2' . The inner border of \mathcal{S}_2' is the border of \mathcal{S}_1' . The outer border is fixed by the conditions that \mathcal{S}_2' has volume V_0 and fully contains all the (and only the) particles that have their gravity centers lying inside \mathcal{S}_2 . The relevant particle number will be denoted by N_2' . In this way one determines, step by step, \mathcal{S}_3' , \mathcal{S}_4' and so on. Provided V_0 be not too small and the density of the system not too high, the procedure ought to work. Assuming this point fully proved, we pass now to evaluate the left hand side of (21). Using (17) and the property that $\varphi_1 + \varphi_2 = 1$ one finds

$$\begin{aligned} \int_V \eta(\mathbf{r}) d\mathbf{v} &= (n_1 - n_2) \left[\sum_{i=1}^N v_p \varphi_2 N_i' - \varphi_1 (NV_0 - \sum_{i=1}^N v_p N_i') \right] = \\ &= (n_1 - n_2) v_p [\mathcal{N}_{V,0} - \varphi_1 NV_0/v_p], \end{aligned} \quad (30)$$

where $\mathcal{N}_{V,0} \equiv \sum_{i=1}^N N_i'$ represents the number of particles contained within V while $\bar{N}_0 \equiv \varphi_1 NV_0/v_p$ represents the mean number of particles contained within V as this becomes infinitely large. [It is noted that one needs to know φ_1 in order to know \bar{N}_0 .] Subscript 0 recalls that both $\mathcal{N}_{V,0}$ and \bar{N}_0 values depend on the V_0 choice. By (30) it follows that

$$\begin{aligned} \frac{1}{V} \left[\int_V \eta(\mathbf{r}) d\mathbf{v} \right]^2 &= (n_1 - n_2)^2 v_p^2 \frac{[\mathcal{N}_{V,0} - \varphi_1 NV_0/v_p]^2}{NV_0} \approx \\ &= (n_1 - n_2)^2 v_p^2 \lim_{N \rightarrow \infty} \frac{(\mathcal{N}_{V,0} - \bar{N}_0)^2}{NV_0}. \end{aligned} \quad (31)$$

By the same argument used above equation (14), one has that $(\mathcal{N}_{V,0} - \bar{N}_0) = O(N^{1/2})$. and one can therefore write

$$\lim_{N \rightarrow \infty} \frac{(\mathcal{N}_{V,0} - \bar{N}_0)^2}{NV_0} = \frac{1}{v} \quad (32)$$

where, by dimensional analysis, v is a typical volume that must be independent on V_0 for consistency. [This implies that the numerator in the left hand

side of (32) is linear in V_0 .] The left hand side of (32) can be looked at as a procedure able to evaluate the mean particle number fluctuation in the case of physical samples made of fixed and rigid particles of the same volume but not necessarily of the same shape, provided φ_1 be known.

iii) statement C) can simply be applied to an ideal simple cubic crystal to conclude that $I_V(0^+) = 0$. In fact, one approximates the atoms at the centers of the cells by hard bodies of fixed shape and volume v_0 . Denoting the cell size by a , the unit cell volume is $V_c \equiv a^3$. The sequence of cubes V_k , having the same gravity center and orientation, and size edges equal to $(2k+1)a$, is such that the limit of V_k as $k \rightarrow \infty$ is equal to the volume of the infinitely large sample. We name phase 1 that formed by the hard bodies. Then, $\varphi_1 = v_0/V_c$ and equation (23) yields

$$\frac{1}{V_k} \int_{V_k} \rho_1(\mathbf{r}) d\mathbf{v} = \frac{(2k+1)^3 v_0}{(2k+1)^3 V_c} = \varphi_1. \quad (33)$$

The rhs does not depend on k and one finds that $\int_V \rho_1(\mathbf{r}) d\mathbf{v}/V = \varphi_1$ which shows that no $O(V^{1/2})$ contribution is present. Thus, $\rho = 0$ and, consequently, $I_V(0^+)$ is equal to zero for simple cubic crystals. We refer to Gommès (2016) for further geometries characterized by vanishing $I_V(0^+)$ values.

Conclusions

Since physical systems obey properties A) and B), a physical scattering density fluctuation must asymptotically behave according to equation (14) or to (18) and (20) in the case of samples made up of two homogeneous phases. This result can be put in a form similar to Porod's law in the sense that the plot of $(V^{1/2} \int \eta_V(\mathbf{r}) d\mathbf{v})$ versus V shows a plateau of height ν (both positive and negative) at large V s. The practical application of this procedure is however much more ambiguous than in Porod's cases (Ciccariello *et al.*, 1988) unless $\eta(\mathbf{r})$ is analytically known, a very exceptional case indeed. In most of the cases, $\eta(\mathbf{r})$ is generated by numerical simulations over a rather small spatial domain and, consequently, the application of the above recipe does not yield fully consistent results. The three panels of Fig.1, reported for greater completeness, illustrate these aspects. They refer to the simplest case of N random points x_i uniformly generated within the interval $[0, 1]$ with the further constraint that their relative distance are greater than $\sigma \equiv \varphi_1/N$. We set $\varphi_1 = 0.2$ and considered the cases: $N = 10^3$, 10^4 and 10^5 . Since the value of σ decreases as N increases, the onset of the asymptotic behavior ought be more evident in the case $N = 10^5$, as it really happens. For this reason, the shown panels refer to $N = 10^5$. In the upper panel, we have

interpreted the segments $[0, x_1]$, $[x_2, x_3]$, $[x_4, x_5], \dots$ and $[x_1, x_2]$, $[x_3, x_4], \dots$ as those respectively relevant to phases 1 and 2. Starting from the origin we evaluated the mean value $\bar{\rho}_L$ of $\rho_1(x)$ over the interval of length L . Fitting the resulting values to the function $\varphi + \rho_0 L^{1/2}$ in the range $0.5 < L < 1$, we determined both φ and ρ_0 . In particular the resulting value $\varphi = 0.5004$ looks quite accurate owing to the uniform distribution of the x_i s. The panel shows the plot of the resulting $L^{1/2}(\bar{\rho}_L - \varphi)$ quantity. The approach to a plateau appears evident. The lower two panels refer to a different model obtained by the generated x_i s, since each of these points is interpreted as the center of an interval of length σ . These intervals form phase 1 and the complement of their union with respect to interval $[0, 1]$ phase 2. The bottom left panel

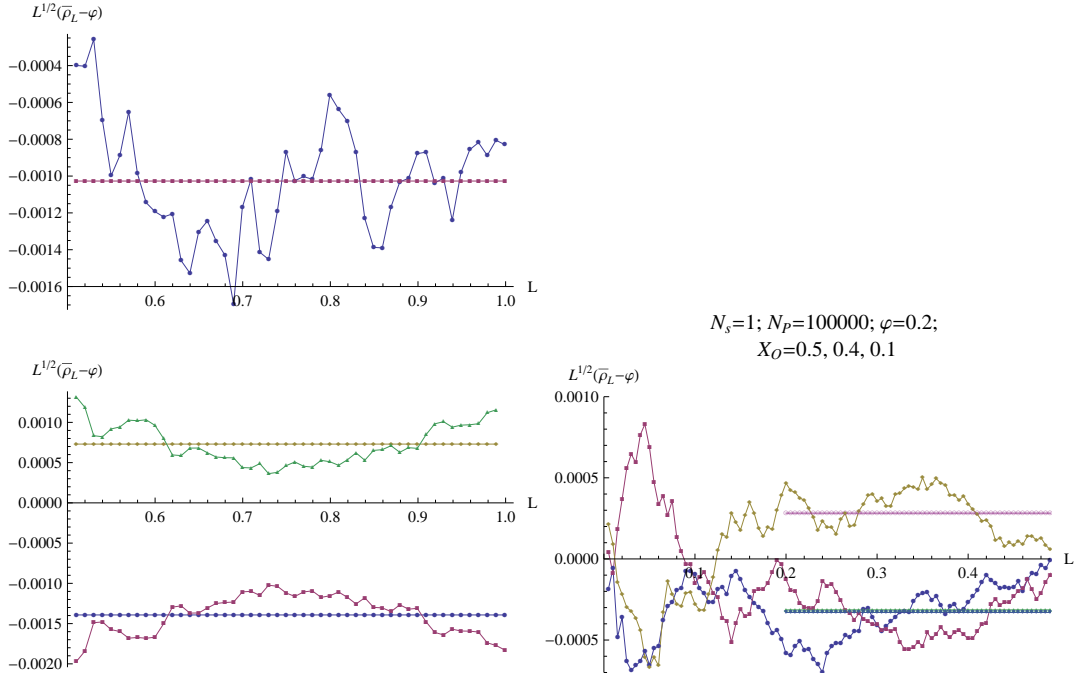


Figure 1: The three panels numerically illustrate the approach of one-dimensional random generated scattering densities to the theoretical behavior predicted by equations (18) and (20).

shows the behavior of the fitted $L^{1/2}(\bar{\rho}_L - \varphi)$ quantities for phase 1 (bottom red curve) and phase 2 (top green curve). In the two cases the values of φ , resulting by the fits, are respectively 0.1998 and 0.7995, quite close to the exact 0.2 and 0.8 values. The corresponding ρ_0 values are the plateau heights. They ought to be opposite while they are -0.00138 and 0.00086 and thus the condition is only weakly obeyed. The last panel (bottom right) checks the independence of the mean values if one chooses different origins.

The blue, red and golden curves refer to origins sets at $X_0 = 0.5, 0.4$ and 0.1 . To attain the value $L = 1/2$ in the three cases, the x_i sequence was periodically replicated on the left and on the right. In the nearly asymptotic range $L > 0.2$, the plateau heights were determined by the the expounded best-fit. In contrast to the choice $X_0 = 0.1$, going from $X_0 = 0.5$ to $X_0 = 0.4$ can be considered a small shift since the plateau does not appreciably change. This conclusion is not unexpected when the scattering density is generated on a finite interval. Overall, the shown cases confirm the difficulty in numerically applying relations (14) or to (18) and (20), though the usefulness of the relations to better characterize physical scattering density cannot be denied on a theoretical ground.

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Appendix A: proof of equation (14)

Equation (13) is equivalent to

$$\lim_{V \rightarrow \infty} \left(\left| \int \eta_{V_O}(\mathbf{r}) d\mathbf{v} \right| / V^{1/2} \right) = |\nu|, \quad (34)$$

Let us first keep O fixed. The limit mathematical definition ensures that, for any $\epsilon > 0$, implies that the absolute value of the difference of the two sides of (34) is smaller than ϵ if $V > V_\epsilon$. Choosing ϵ in such a way that $\epsilon < |\nu|$, one concludes that the left hand side of (34) is positive for all the sets V_O of volume greater than V_ϵ . Consequently for all the V_O s such that $V > V_\epsilon$ the sign of $\int \eta_{V_O}(\mathbf{r}) d\mathbf{v}$, that continuously depends on V_O , is either positive or negative because the integral never vanishes. One can therefore write

$$\int \eta_{V_O}(\mathbf{r}) d\mathbf{v} \approx \nu_o V^{1/2}, \quad \text{with} \quad |\nu_o| = |\nu|. \quad (35)$$

The assumption of a fixed O is now removed. Consider a different origin O' . The above reasoning holds true provided ν_o is substituted with $\nu_{o'}$. The absolute values of these two constants are equal. Hence, either $\nu_{o'} = \nu_o$ or $\nu_{o'} = -\nu_o$. Let O span all the space. This divides into two regions. The first is formed by all the O' such that $\nu_{o'} = \nu_o$ and the second by the O' such that $\nu_{o'} = -\nu_o$. Consider now two origins O_1 and O_2 , very close to each other and respectively lying within the first and second region. Let O denote the center

of a set V_O and let O continuously move from O_1 to O_2 . Besides let the V_O 's volume be so large that the integral obeys to its asymptotic behavior. The integral continuously depends on the O position. This property is clearly contradicted by the fact the the asymptotic leading term takes opposite values as O goes from O_1 to O_2 . This proves that equality $\nu_{o'} = -\nu_o$ cannot occur and eqaution (14) is proved.

We conclude this section reporting an example of scattering density fluctuation that obeys condition (14). Consider first the one dimensional case and the function

$$F_\eta(x) \equiv \sin^2(x)/|x|^{1/2}. \quad (36)$$

By MATHEMATICA software (Wolfram Research, Champaign, IL, USA) one finds that

$$\int_a^{a+L} F_\eta dx = (a+L)^{1/2} - a^{1/2} + (\pi/2) \left(\mathcal{C}(2(a/\pi)^{1/2}) - \mathcal{C}(2((a+L)/\pi)^{1/2}) \right), \quad (37)$$

where $\mathcal{C}(\cdot)$ is the cosine Fresnel integral (Abramowitz & Stegun, 1970). Its leading asymptotic expansion at large L simply reads

$$\int_a^{a+L} F_\eta dx = L^{1/2} \left(1 + [\pi^{1/2} \mathcal{C}(2(a/\pi)^{1/2})]/2 - a^{1/2} - \pi^{1/2}/4 \right) / L^{1/2} + o \quad (38)$$

and it agrees with the one dimensional version of (14). By this result it is trivial to show that the function $F_\eta(x)F_\eta(y)F_\eta(z)$ obeys (14) and, therefore, represents a candidate for a physical scattering density fluctuation.

Appendix B: an example of random sequence obeyng (27) and (28)

We explicitly show that both condition (27) and (28) must be fulfilled for (25) to be fulfilled . To this aim, we assume that the ξ_i s, defined below equation (23), have the form

$$\xi_{3j-2} = a j^s + j^{-r}, \quad \xi_{3j-1} = -a j^s + j^{-r} \quad \text{and} \quad \xi_{3j} = j^{-r}, \quad (39)$$

with $r > 0$, $-1 < s < 1$ and $j = 1, 2, \dots$. Put

$$S_{3N} \equiv \sum_{j=1}^N (\xi_{3j-2} + \xi_{3j-1} + \xi_{3j}) \quad (40)$$

$$\text{Var}_{3N} \equiv \sum_{j=1}^N (\xi_{3j-2}^2 + \xi_{3j-1}^2 + \xi_{3j}^2) / 3N. \quad (41)$$

MATHEMATICA yields

$$S_{3N} = 3 H_N^{(r)} \quad \text{and} \quad \text{Var}_{3N} = \left(3 H_N^{(2r)} + 2 a^2 H_N^{(-2s)} \right) / 3N, \quad (42)$$

where $H_N^{(r)}$ denotes the generalized harmonic number function (Erhardt, 2016). The leading asymptotic expansions, with respect to N , of S_{3N} and Var_{3N} are

$$S_{3N} \approx 3 N^r \zeta(r) + 3 N^{1-r} / (1-r) + 3 / (2N^r) \quad (43)$$

and

$$\text{Var}_{3N} \approx \begin{cases} \frac{2a^2 N^{2s}}{6s+3} + \frac{\zeta(2r)}{N} + \frac{2a^2 \zeta(-2s)}{3N} + \frac{1}{(1-2r)N^{2r}} & \text{if } r \neq 1/2, \\ \frac{2a^2 N^{2s}}{3(1+2s)} + \frac{3\gamma_C + \log(N) + 2a^2 \zeta(-2s)}{3N} & \text{if } r = 1/2. \end{cases} \quad (44)$$

where $\zeta(\cdot)$ denotes the Riemann zeta function and γ_C the Euler-Mascheroni constant. Equation (43) shows that, whatever s , S_{3N} behaves as \sqrt{N} if and only if $r = 1/2$ while, for different rs , it increases faster. Equation (44) shows that Var_{3N} diverges with N if $s > 0$. Hence, if $s > 0$ and $r = 1/2$, the left hand side of (28) also must diverge to cancel the variance divergence because (25) is $O(N^{1/2})$. If $s = 0$, the variance is finite and, therefore, sum (28) diverges faster than \sqrt{N} if $r \neq 1/2$ and exactly behaves as \sqrt{N} if $r = 1/2$. The above conclusions also apply to S_{3N+i} and Var_{3N+i} with $i = 1, 2$ and are, therefore, fully general.

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